Letter to the Editor

Comment on the use of phenols as probes for the kinetics of heterogeneous photocatalysis

Phenols have frequently been used to probe the efficiency of heterogeneous photocatalysts. Numerous different substituted phenols have been employed for this purpose and the efficiency has been quantified by measuring the consumption of phenol as a function of time [1–5]. An interesting observation for phenolic probes is that the rate of consumption in a given photocatalytic system depends on the nature (*i.e.* substituent pattern) of the phenol [6–8]. However, for all phenols, oxidation by the excited photocatalyst or the subsequently produced hydroxyl radical is a highly exothermic process [9,10]. For this reason, the substituent dependence would appear to be slightly unexpected assuming oxidation of the phenol/phenolate to be the rate determining step. This also indicates that phenols are of limited use when assessing the general efficiency of photocatalytic systems. To be able to compare studies using different phenols and the photocatalytic efficiency derived from these studies, it is essential to fully account for the degradation mechanism of the probe and to focus at initial degradation rates that are not influenced by the presence of degradation products. The purpose of this communication is to shed some light on the degradation of phenols and substituent effects on the mechanism of this process.

In order to qualitatively and quantitatively describe photocatalytic systems, numerous kinetic models have been developed [11–17]. Due to the high abundance of experimental data on phenolic compounds in the literature, data on phenols have been used to benchmark some of the models [13,14,17–19]. Fairly recently, a new kinetic model was presented where a back reaction (the oxidized species is reduced back to its original state by the photocatalyst) is incorporated to account for experimental observations made in some studies [13]. In particular, this model is claimed to describe the kinetics of phenol photo-degradation better than other models.

Indeed, kinetic models are very useful for the understanding of the process itself and for the design of reactors for heterogeneous photocatalysis. However, it is essential that the chemistry of the probe is properly accounted for.

One-electron oxidation of phenols leads to the formation of phenoxyl radicals (reaction 1) (Scheme 1).

In oxygen-free aqueous solution, the phenoxyl radical can undergo radical-radical combination reactions to produce a dimer (reaction 2). This leads to consumption of the phenol (Scheme 2).
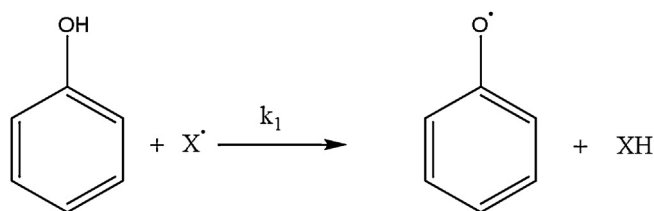
Oxygen present in the aqueous solution does not interact with the phenoxyl radical and thereby does not influence the consumption of the phenol [20]. However, oxygen present in a heterogeneous photocatalytic system will be reduced to superoxide by the conduction band electron produced upon photo excitation of the photocatalyst [21]. This process enhances the efficiency of the photocatalyst due to the removal of electrons that could otherwise recombine with the positive hole [22]. It has long been known that superoxide reacts with phenoxyl radicals by electron-transfer and by radical-radical combination (reaction 3 and 4) [10,23] (Scheme 3).

The electron-transfer process yields phenol/phenolate and molecular oxygen. Hence, this process counteracts the consumption of phenol in the system. With reference to the new kinetic model mentioned above [13], this is a back reaction that does not directly involve the photocatalyst. The radical–radical combination reaction between the phenoxyl radical and superoxide is irreversible and leads to subsequent ring-opening and loss of aromaticity, *i.e.* consumption of the phenol. To the best of our knowledge, the competition between reaction 3 and 4 is not accounted for in the benchmarking of kinetic models for heterogeneous photocatalysis. In fact, none of the reactions leading to irreversible consumption of phenol are included. Not including the well-known chemistry of phenoxyl radicals in aqueous solution containing superoxide renders the inclusion of new and unverified processes to fit experimental results meaningless.

Interestingly, the competition between reaction 3 and 4 has been systematically studied using pulse radiolysis about two decades ago [10]. It turned out that the fraction of electron-transfer (*i.e.* back reaction) is strongly dependent on the redox properties of the phenoxyl radical [10]. For phenoxyl radicals with high reduction potential (corresponding to phenols that are more difficult to oxidize), the fraction of electron transfer is higher than for phenoxyl radicals with low reduction potentials (corresponding to phenols that are more easily oxidized). This can roughly be described to follow a linear free energy relationship. In general, the properties and reactivity of phenoxyl radicals have been shown to follow Hammett type linear free energy relationships using Brown σ^+ substituent constants [9,24]. Both the standard reduction potentials of substituted phenoxyl radicals and the homolytic O—H bond dissociation enthalpies of substituted phenols are linearly correlated to the Brown σ^+ substituent constant. The correlations are valid also for multi-substituted phenols and phenoxyl radicals [24]. This enables us to analyze some of the results reported for photocatalytic systems where substituted phenols have been used as probes.
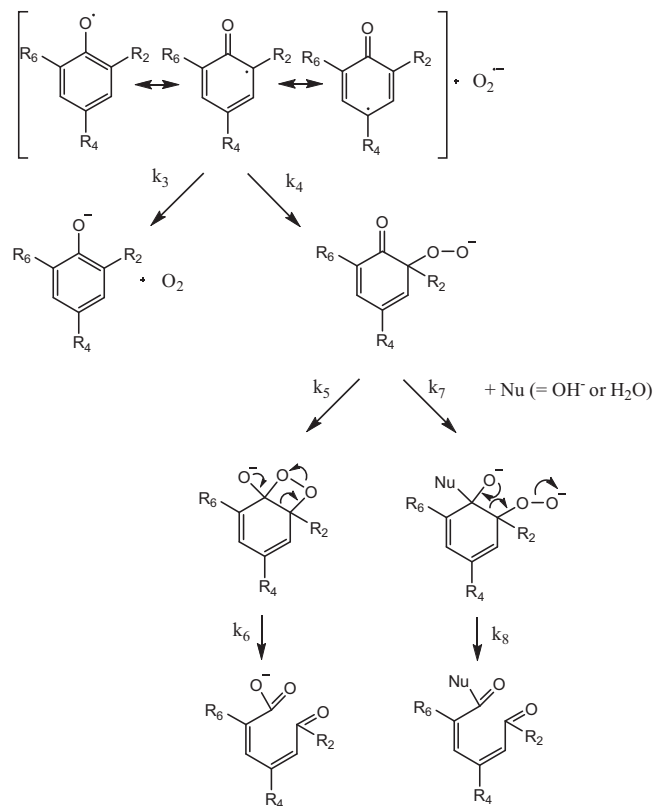
Serpone et al. [5] have used a series of substituted phenols to determine the photocatalytic efficiency of TiO_2. Their results clearly show that the photocatalytic efficiency of a given system varies by a factor of three depending on the structure of the phenol. Applying the linear free energy relationships described above, we can plot the relative photocatalytic efficiency against the sum of the Brown substituent constants (for multisubstituted phenols). This is
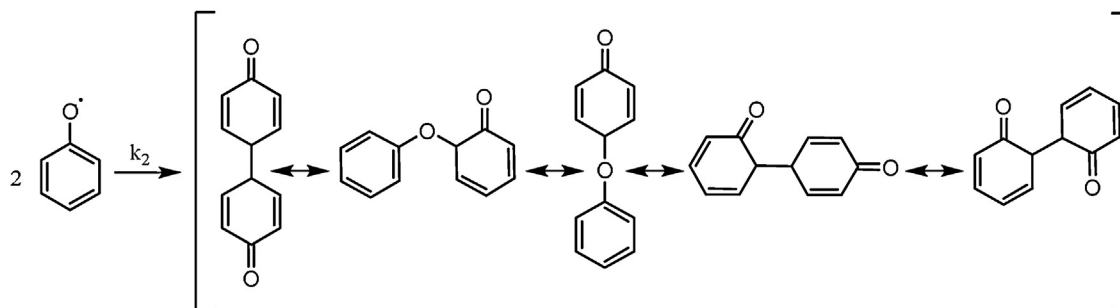
Scheme 1.

comparable to plotting the relative photocatalytic efficiency against the standard reduction potential of the phenoxyl radicals. The resulting plot is given in Fig. 1.

As can be seen, there is a significant substituent effect on the relative photocatalytic efficiency and there is also a fairly good correlation between the relative photocatalytic efficiency and the sum of the Brown substituent constants for each phenol. The relative photocatalytic efficiency decreases linearly with increasing standard reduction potential (more positive Brown substituent constant) of the phenoxyl radical. The same trend was observed in a study on photocatalytic degradation of chlorophenol and nitrophenol [25]. The standard reduction potential of the nitrophenoxyl radical is significantly higher than that of the chlorophenoxyl radical [9] and chlorophenol is consequently significantly more rapidly decomposed than nitrophenol. This is exactly what we would expect from the trend observed for the reaction between phenoxyl radicals and superoxide. Hence, it is clear that the inclusion of the complete reaction scheme for phenoxyl radical chemistry is required for kinetic models for heterogeneous photocatalysis when benchmarking against experimental results where phenols have been used as probes.

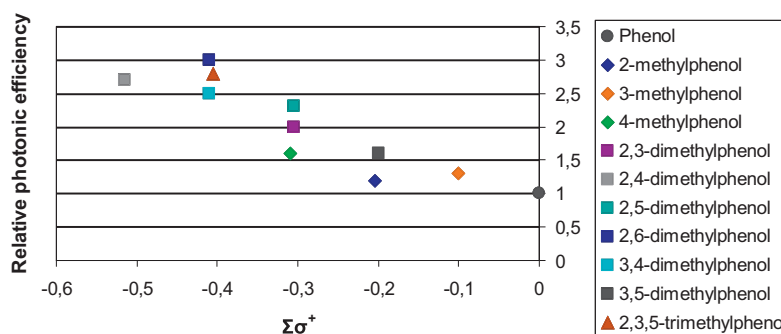**Scheme 3.**

Scheme 2.

Fig. 1. Relative photonic efficiencies for different phenolic substances [5] plotted against the Brown substituent constants. Phenol is the standard reference. The initial scavenger concentration is approximately 200 μmol L^{-1}, [TiO$_2$] = 2 g L^{-1} and pH = 3.0.

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